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WITH ONE PLATE.

INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED WITH AID FROM THE RUMFORD FUND.

(Continued from page 3 of cover.)

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Synopsis.

Absorption of ultra-violet light by the lower atmosphere.—Photographs of the spectrum of a Cd spark, in the interval λ3500–2500 were taken from several stations where the air path ranged from 160 to 8000 meters. The apparent absorption for the shorter wave-lengths was very marked as the distance between the source and the spectrograph increased. A method of photographic photometry, similar to that devised by Stetson to determine stellar magnitudes, was used to measure the changes in relative intensities of the lines as the air path was increased. The values of the relative intensities of the spectral lines were plotted with the curve for molecular scattering computed from the Rayleigh formula. The results agree with Strutt's work in showing that the ozone concentration in the lower region of the atmosphere is negligible but molecular scattering will not explain the magnitude of the effect as has been previously supposed. The absorption of light in this region of the spectrum by long columns of oxygen and loss by ionization of the air may account for the observed attenuation.

Introduction.—It has long been known that the ultra-violet solar spectrum ends quite abruptly near λ2900. Cornu [1] found that the limit depended upon the altitude of the sun and concluded that the earth's atmosphere was the cause of the apparent absorption. On the assumption that the concentration of the absorbing material did not change with altitude, Cornu calculated the amount the spectrum should be extended with increase in altitude. He then made observations at several stations from sea-level to a height of 2560 meters and obtained experimental results in accord with this amount.

About the same time Hartley [2] was studying a number of gases to get information on absorption spectra. He photographed ultra-violet spectra after the light had been transmitted through measured quantities of gas at atmospheric pressure. The oxides of nitrogen, CO_2,

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1 Cornu, Journ. de Physique, 10, 1881.
2 Hartley, Journ. Chem. Soc., 39, 1881. Nature, p. 475, 1889.

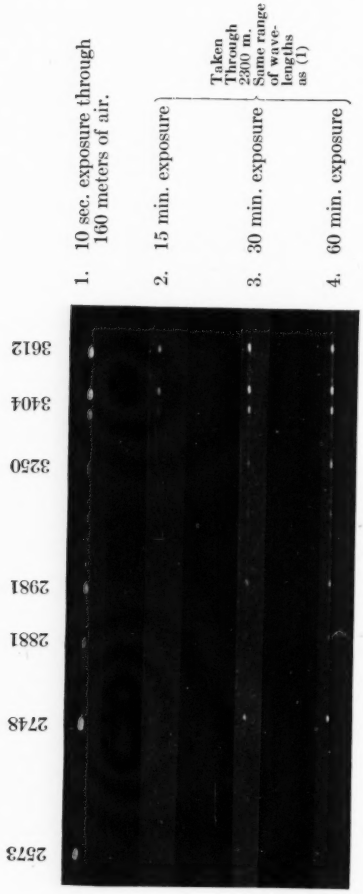
NH_3, H_2O_2, and water vapor showed no appreciable absorption in this region even in far greater quantities than occur in the atmosphere. Ozone, when very dilute, showed an absorption band of great intensity extending from λ2850 to λ2320. The limit of transmission was finally restricted to λ3160 in presence of greater quantities of the gas. Hartley concluded that ozone in the atmosphere is the absorbing factor which accounts for the limit of the solar spectrum, since he found an indication of ozone in free country air. He also presented some evidence to show that the concentration of ozone at higher altitudes is greater than at sea-level.

In repeating Cornu's experiments on the limit of the solar spectrum, Miethe and Lehmann [3] found no change in the ultra-violet limit when the altitude was varied by 4500 meters. Wigand,[4] taking special precautions to prevent fog on the photographic plate, took the apparatus used by Miethe and Lehmann to an altitude of 9000 meters in a balloon. Confining his attention to the last trace of light action recorded on the plate, he found the limit to be λ2896 and the difference in the limit at this great altitude and at Halle, near sea-level, to be inappreciable.

In view of these conflicting results, it seemed worth while to investigate the absorption of long columns of air near the earth's surface,[5] for under these conditions the uncertainties as to the composition of the absorbing layer are largely eliminated. Work was begun in 1916 but suffered several unavoidable delays. During the progress of the research Strutt [6] published the results of his investigations on the same subject; the conclusions arrived at in this paper do not materially differ from his, but the author was able to express the magnitude of the effect in quantitative terms and to show that molecular scattering does not explain the observed absorption.

In the present investigation the spark spectrum of Cd was photographed through columns of air from 160 meters to 8000 meters. By comparing the measured opacities of the plates thus obtained with the opacities produced in the laboratory when the air path was small, the changes in the relative intensities of the principal Cd lines in the ultra-violet were obtained. These changes in intensities give a measure of the absorption due to the column of air under examination. As the results did not point to the presence of ozone as the dominating factor

3 Miethe and Lehmann, Ber. Preuss. Akad. Wissens., 8, p. 268, 1909.
4 Wigand, Physik. Zeits., 14, p. 1144, 1913.
5 Lyman, Monthly Weather Review, 42, 8 August, 1914.
6 Strutt, Proc. Roy. Soc., London, 94A, p. 260, 1918.


1. 10 sec. exposure through 160 meters of air.
2. 15 min. exposure
3. 30 min. exposure
4. 60 min. exposure
Taken Through 2300 m Same range of wave-lengths as (1)
3612
3404
3250
2981
2881
2748
2573

and as the effect of scattering may well be important, these relative intensities were plotted with the computed curves for molecular scattering. The details of the procedure follow.

Procedure.—Over a hundred photographs of the ultra-violet spectrum of a Cd spark were taken between January 1916 and November 1917, at varying distances from the source. Nearly all the work was done on the clearest nights so as to avoid the long exposures caused by haze. The spark between Cd terminals in parallel with a suitable capacity was produced by a half kw. transformer on a 60 cycle, 110 volts circuit. The apparatus for photographing the spectra consisted of an objective prism arrangement,— a box containing a large 60° quartz prism, a quartz lens about 8 cm. in diameter, of approximately one meter focal length, mounted directly back of the prism, and a holder for the photographic plate. An open tube about 60 cm. long, 10 cm. in diameter was mounted in front of the prism and several diaphragms were inserted along the path of the light to prevent stray radiation from reaching the photographic plate. A small telescope was attached permanently to the box to aid in getting the apparatus in line with the distant source. The adjustment, once made, was not changed until a number of photographs had been taken.

The images are recorded as small spots as shown in the accompanying photographs. (1) shows the spectrum of the Cd spark $\lambda 3612$–$\lambda 2573$ through 160 meters of air obtained by a 10 seconds exposure. (2), (3), and (4) were all taken on the same plate on an exceptionally clear night through 2300 meters of air, the exposure being 15, 30 and 60 minutes respectively. A number of exposures were then made through an air path of 8000 meters. On several plates of 4 hours exposure $\lambda 2573$ was recorded through this long path of air but the images were very faint. Strutt has already published photographs of mercury vapor spectrum through about 6500 meters which show the same result.

Although many photographs were taken, only a few nights in a year are really satisfactory for this work. A short rain followed by a dry Northwest wind seemed to leave the air in the best condition.

A large number of exposures were made in the laboratory also with an air path of two or three meters. The same plate, Seed 30, emulsion 15511, and the same development were used throughout the work. By using a diaphragm in the collimator the exposure times as well as the opacities given in (2), (3) and (4) were approximately reproduced. In the case of plates for the five mile air path, it was found that the less refrangible end of the spectrum was over-exposed so badly in order to

get a record of the shorter wave-lengths, that no satisfactory measurements of opacities could be made on them, except for a very limited range of wave-lengths. The opacities in this case for λ3404 were considerably greater than for the same wave-length recorded through 2300 meters of air while for λ2748 and λ2573 the opacity was much less than for that wave-length recorded through the shorter distance. However, the plates for the 2300 meters distance give quite a definite idea of the effect. These exposures were taken with the spectograph at Jefferson Physical Laboratory and the source of light at the Chapel at Tufts College.

The decrease in intensity for the shorter waves may be seen by comparing the opacities of the plates for the different spectral images obtained with a long air path, with the corresponding opacities produced when the air path between the source and the plate is negligible. If I_1 is the intensity of the light which reaches the photographic plate for a given wave-length λ_1, and I_2, the same for light of shorter wave-length λ_2, then the ratio I_2/I_1 for the case with a long air path is less than the same ratio for a short air path. The ratio is different because the apparent absorption is greater for the shorter wave-lengths. This can easily be seen by direct comparison of exposures (1) and (4). If $R = I_2/I_1$ is the ratio of the intensities of these two lines as produced in the laboratory when the air path is negligible, and $R' = I'_2/I'_1$ is the ratio for the long air path, then R'/R gives the relative intensity of the light of shorter wave-length after passing through the long column of air, compared with the intensity of λ_1. This value of R'/R was determined from the opacities produced on the photographic plates for the principal lines in the ultra-violet spectrum of Cd, λ3404 being used as the standard. The absorption for light of wave-length greater than λ3404 was found to be small and this line was most suitable since the opacity of the silver deposits for this wave-length was not too great to be easily measured.

Photometric method.—The notation generally accepted in photographic photometry [7] is used in this paper. $D = \log O$, $D = K \log E$ and $E = It^p$ where D is the density of silver deposit, O the opacity, K a constant, E the exposure, I the intensity of the light which acts for t seconds and p is a constant.

The opacities were measured with Dr. Stetson's [8] apparatus for determining stellar magnitudes. In this apparatus the photographic

[7] Sheppard and Mees, Investigations on the Theory of the Photographic Process, (Longmans), p. 45.

[8] Stetson, Astrophysical Journal, 43, p. 253, 1916.

plate is placed emulsion side down over a small diaphragm, through which light passes from a standard source. The light is then brought to a focus on one junction of a Bi-Ag thermo-couple connected to a sensitive galvanometer. The deflections of the galvanometer, when the diaphragm is covered by the spectral image and when it is covered by the clear plate near the image, give a means of eliminating the effect of fog on the plate and of getting a quantity proportional to the capacity.

If d is the galvanometer deflection when the image is over the diaphragm, and d' the deflection for the clear plate, then $= \frac{d' - d}{d'}$ is proportional to the opacity, $c\delta = O$. The density of the silver deposit, $D = \log O$, is proportional to the logarithm of the exposure, $D = K \log E$. So we have $(c\delta)^{\frac{1}{k}} = E$. Within certain limits we may write $E = It^p$ where p is a quantity which must be determined by experiment, as it is a factor of the plate and over any considerable variation of I is by no means constant. Over the range of time and of wave-lengths used p was found to be approximately 0.92.

In order to determine the range over which the densities were proportional to log time, the values of δ, from the galvanometer readings for $\lambda 3404$ taken from a number of plates made in the laboratory, were plotted against log t, where t varied from one to thirty minutes. It was found that between $\delta = 0.30$ and $\delta = 0.65$ for this wave-length the curve was practically a straight line, the complete curves resembling the familiar D, log E curve. Similar curves were made for the spectral images of the other Cd lines. Since $\delta = 0.50$ falls very near the middle of the straight portion of each of these curves, the corresponding values of log t necessary to produce this particular value of δ for the different wave-lengths, give a means of calculating the intensities of the Cd lines. Of course the spectral sensitivity of the plate enters into the problem here. If the time required for $\lambda 3404$ to register $\delta = 0.50$ is taken as a standard, then the time required for $\lambda 2881$ to register $\delta = 0.50$ must contain a factor a which depends upon the change of sensitivity with wave-length. For the same values of δ, since $(c\delta)^{\frac{1}{k}} = It^p$, we have for two different spectrum lines $R = I_2/I_1 = (t_1/at_2)^p$. Then $R'/R = \left(\frac{t'_1\, t_2}{t'_2\, t_1}\right)^p$ gives the transmission of λ_2 through a long column of air compared to the transmission of λ_1 as a standard. Since only ratios are desired, the factor a expressing the spectral sensitivity of the plate drops out.

In the ratio $R'/R = \frac{I'_2 I_1}{I'_1 I_2} = \left(\frac{t'_1 t_2}{t'_2 t_1}\right)^p$, I_1 is the intensity of λ3404 for the exposures in the laboratory where the radiation suffers no appreciable absorption, I'_1 the intensity of λ3404 after passing through 2300 meters of air, and I_2 and I'_2 are in turn the corresponding intensities for the lines λ3250, 2981, 2881, 2748, and 2573.

Molecular scattering.—It will be shown below that ozone absorption has little if any effect on I'_1 and I'_2 but it is known that molecular scattering plays an important part. The problem of the scattering of light by small particles was studied by Lord Rayleigh more than forty years ago. If i_0 is the initial intensity of the light, then the intensity, i, after passing through a scattering medium of thickness x is given by the equation $i = i_0 e^{-Kx}$, where K is the coefficient of scattering. Rayleigh first calculated the value of K on the basis of the elastic solid theory and found,

$$K = \frac{32\pi^3(\mu - 1)^2}{3N\lambda^4},$$

where μ is the index of refraction for the light of wave-length λ, and N is the number of particles per cubic centimeter of air at N.T.P. The same result was obtained by Rayleigh [9] later from the electromagnetic theory, and Schuster [10] and recently King,[11] by quite different methods, have also arrived at this result. The formula has been tested experimentally by several investigators and found satisfactory. The observations of Dr. C. G. Abbot [12] on the intensities of sunlight at Mt. Wilson and at Washington, D.C. agree very well with the values calculated for molecular scattering according to the above formula.

It is necessary then to correct the intensity of the standard after the light has passed through a considerable layer of air. Using the Rayleigh formula, the calculated amount of scattering for light of wave-length λ3404 is 16% in the air path under consideration. Consequently, the value 0.84 is taken as the intensity of λ3404 after passing through 2300 meters of air. For instance, consider a line of shorter wave-length whose intensity appears to be equal to the standard when the air path is small, then if the measured opacities show this line to be

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[9] Rayleigh, Phil. Mag., 47, p. 375, 1899.
[10] Schuster, Theory of Optics, p. 325.
[11] King, Phil. Trans. Roy. Soc., London, 212A, p. 375, 1913.
[12] Abbot, v. (10). Ann. Astr. Abs. Smithsonian Inst. 2, p. 113, 1908.

one-half the intensity of λ3404 after passing through a long column of air, the intensity of the line of shorter wave-length is taken as one-half of 0.84. The results obtained in this way are plotted in Figure 1 with the computed curves for scattering.

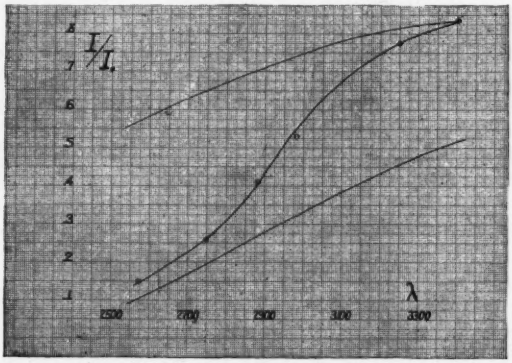

FIGURE 1. The lower curve shows the effect of molecular scattering calculated from Rayleigh's formula for an air path of 8000 meters at N.T.P. — an equivalent to the earth's total atmosphere. The upper curve shows the same for an air path of 2300 meters at N. T. P. The points plotted between these curves were obtained from the measured opacities of the spectral images.

The decrease in intensity for the shorter wave-lengths, as found in my experiments, is very marked. In view of the results obtained by Fabry and Buisson [13] on the absorption of ozone and the recent work by Fowler and Strutt [14] on the absorption bands in the ultra-violet spectra of the sun and a number of stars of different spectral types, this deviation from the scattering curve can hardly be attributed to ozone absorption. The Cd lines λ2748, 2573 and 2313 seem normally to have about the same intensity. λ2573 lies very near the maximum of the great absorption band of ozone in the ultra-violet region,— a path of 1.2 cm. of 1% ozone suffices to absorb it completely, while λ2748 and λ2313 are only slightly diminished. If atmospheric ozone were the chief factor in the apparent absorption, indicated by a long

[13] Fabry and Buisson, Comp. Rend., 156, p. 782, 1913. Journ. de Physique, 3, p. 196, 1913.
[14] Fowler and Strutt, Proc. Roy. Soc., London, 93A, p. 577, 1917.

air path, λ2313 would be shown stronger than λ2573. In no case did this occur. Photographs taken for the five mile distance agree with the work of Strutt in showing that a concentration of ozone in the air near sea-level greater than 10^{-8} is improbable. Chemical determinations give results over a thousand times this amount, but the difficulties of such determinations are very great and the data given by several observers differ widely.

Evidently, the problem of the effect of our atmosphere on ultra-violet light has been resolved into two parts. The first calls for an explanation of the abrupt termination of the solar spectrum in the ultra-violet, the second calls for an explanation of the deviation of the intensity of a distant terrestrial source from the curve calculated from a consideration of molecular scattering.

Properties of Ozone.—The limit of the solar spectrum is certainly set by ozone absorption. From the chemical and physical properties of ozone, there is reason to believe that there is a fair concentration of that gas probably in the isothermal layer of our atmosphere where the mean temperature is about −55° C and the pressure about 250 m.m. Ozone is quite stable at this low temperature and although the stability decreases with decreasing pressure the effect is not very large until the pressure [15] is below 100 m.m. It is also important to note here that ozone is produced quite rapidly by light of wave-length less than λ2000, but is slowly recombined by light of longer wave-length. Accordingly, light of wave-length less than λ2000 coming from the sun, forms ozone in the higher layers of our atmosphere. This ozone should be found in higher concentration in the isothermal layer since the conditions of temperature and pressure are the most favorable there.[16] Such a layer of ozone would account for all the observed facts on the absorption of sun-light in the region above λ2000.

The data collected by several observers on the ozone content at varying altitudes [17] are in fair agreement in showing a gradual increase up to 3600 meters. Pring [18] gives average values obtained by sending his apparatus up as high as 20,000 meters in Hydrogen balloons but the results were hopelessly discordant. A greater percentage of the heavier molecules as O_3 should be found at the lower altitudes, but the very rapid recombination of O_3 into O_2 at temperatures found near the surface of the earth and the violent chemical action of ozone on or-

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15 von Bahr, Ann. d. Physik, 33, 3, p. 598, 1910.
16 Warburg, Ber. Preuss. Akad. Wissens., Berlin, 48, p. 1126, 1901.
17 Thierry, Comp. Rend., 124, p. 460, 1897.
18 Pring, Proc. Roy. Soc., London, 90A, p. 204, 1914.

ganic matter would be certain to prevent an appreciable concentration of that gas in the lower atmosphere.

Results.—The result of the present paper shows, first, that the concentration of ozone near the surface of the earth is negligible — as may be expected from the properties of ozone given above; second, the attenuation of ultra-violet light by the lower atmosphere cannot be explained by atmospheric scattering alone. There are several other agents which, no doubt, have some effect. The absorption by a long path of oxygen, and the ionization of the air by the light of wave-length under consideration deserve attention. Sulphur dioxide and methane absorb ultra-violet light, but no data are at hand which show the effect to be important for concentrations of these gases too small to be detected easily by chemical means.

Little is known about the absorption of long columns of oxygen in this region of the spectrum. The effect of oxygen on shorter wave-lengths is well known; Kreusler [19] found that a column of air 20 cm. long absorbed about 9 per cent of the light at λ1860, while he detected no absorption at λ1930. By compressing the gas in a tube, Liveing and Dewar [20] extended the absorption band of oxygen into the longer wave-lengths. In one experiment the spectra of the carbon arc and of the iron spark were photographed through a tube 18 meters long containing oxygen under pressure of 85 atmospheres. Under these conditions the gas was found to be quite transparent for violet and ultra-violet rays to about λ2745. From that point, the light gradually diminished, and beyond λ2664 appeared to be wholly absorbed.

The mass of oxygen used in this experiment is approximately the same as that traversed in a column 8000 meters long at N.T.P., but the absorption is no doubt somewhat more at the higher pressure than for an equal mass at a lower pressure. But the shoulder of the great absorption band in the Schumann region may extend far enough into the longer wave-lengths to affect the intensity of the light appreciably.

The formation of ions by the action of ultra-violet light on air may be important. Bloch [21] found that strong ultra-violet light of wave-length greater than 1800 produced a certain ionization on unfiltered air. Lenard and Ramsauer [22] verified this, but found there was no volume effect on the pure gases of the atmosphere and that the effect on air containing dust depended upon the presence of moisture. No

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19 Kreusler, Ann. d. Phys., 6, p. 412, 1901.
20 Liveing and Dewar, Phil. Mag., 26, p. 286, 1888.
21 Bloch, Comp. Rend., 146, p. 892, 1908.
22 Lenard and Ramsauer, Sitz. Ber. d. Heidelberger Akad. 1910–1911.

results are at hand, however, which show the variation of such an effect with wave-length. All that can be stated is that the photo-electric effect on dust may cause part of the diminution of intensity and the deviation from the scattering curve as recorded in Figure 1.

Conclusion.—It seems that (1) the lower atmosphere is practically free from ozone, (2) molecular scattering alone will not account for the attenuation of the shorter wave-lengths from distant terrestrial sources, (3) absorption by oxygen and ionization of the air may explain the deviation from the curve for molecular scattering, (4) probably the isothermal layer of our atmosphere contains the ozone which sets the limit of the solar spectrum in the ultra-violet.

My thanks are due Professor Lyman for many suggestions and for his aid in securing suitable locations for conducting this work, and Dr. Stetson for the use of his apparatus in measuring the opacities.

JEFFERSON LABORATORY,
Cambridge, February, 1922.